Chapter 9

Some Unitary, Binary, and Ternary Non-TiO_2 Photocatalysts

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Additional information is available at the end of the chapter

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Abstract

Among all kinds of green earth and renewable energy projects underway, semiconductor photocatalysis has received wide interest because it provides an easy way to directly utilize the energy of either natural sunlight or artificial indoor illumination. TiO_2, the most widely used photocatalyst, due to its wide band gap, can only be activated under UV irradiation, and thus, the development of novel semiconductor photocatalysts makes a significant advancement in photocatalytic functional materials. One of the effective strategies to overcome this shortcoming is photosensitizing these wide band gap semiconductors with narrow band gap semiconductors which have proper energy levels. This method can not only improve the photocatalytic activity, due to increasing visible-light-harvesting efficiency, but also can decrease the recombination of the charge carriers, because the formation of *n*–*n* or *n*–*p* heterojunctions between the combined semiconductors can induce internal electric fields between them. In this regard, this review presents some unitary, binary, and ternary non-TiO_2 photocatalysts used for the degradation for organic pollutants and for water splitting.

Keywords: semiconductor photocatalysis, non-TiO_2 photocatalysts, composite photocatalysts, pollutant degradation, photoactivity under UV–Vis or visible light

1. Introduction

Among the various Advanced Oxidation Process methods, semiconductor-mediated photocatalysis has been accorded a great significance in recent times due to its potential to mineralize

a wide range of organic pollutants at ambient temperature and pressures into harmless substances, to produce hydrogen in photocatalytic water-splitting process, and to apply in dye-sensitized solar cells [1–3].

From the simple oxides (e.g., TiO_2, ZnO, WO_3, Fe_2O_3), anatase–TiO_2 is a dominant structure employed for sunlight applications mostly due to its charge carrier handling properties. However, the TiO_2-based photocatalyst cannot effectively absorb visible solar light due to a rather large band gap (>3.2 eV), rendering it of little practical significance for solar energy harvesting. Additionally, pure TiO_2 used during photocatalytic processes has few disadvantages, such as low quantum yield due to a high recombination rate between photogenerated electron–hole pairs, or the need of high-energy photons to activate the semiconductors in the UV region.

Qu et al. [4] pointed that designing of an efficient and stable photocatalysts must follow several critical requirements: (*i*) Semiconductor must have band gap large enough to provide energetic electrons and smaller enough to allow for efficient absorption overlap with the solar spectrum (1.23 eV $\ll E_g \ll$ 3.0 eV, typically >2.0 eV); (*ii*) there must be a mechanism to efficiently drive charge separation and the transportation process; and (*iii*) there must be a mechanism to efficiently drive charge separation and the transportation process.

Because, in most cases, single semiconductors are unlikely to satisfy all these requirements, one of the important issues in the photocatalysis fields is to exploit new combining of some semiconductors to form composites which can improve the efficiency of a photocatalytic system. This fact provides an excellent opportunity to continue developing new materials with higher photocatalytic activity and capable to use the sunlight as a green energy source.

The current review is focused on non-TiO_2 materials with particular emphasis placed on application of these photocatalysts in heterogeneous photocatalysis and insight into explanation the photocatalytic mechanism of the composite photocatalyst. This review is organized into four sections: (1) single-semiconductor photocatalysts for pollutant degradation, (2) single-semiconductor photocatalysts for water splitting, (3) semiconductor composite photocatalysts, and (4) conclusions and perspectives.

2. Single-semiconductor photocatalysts for pollutant degradation

In general, fundamental principles of photodegradation mechanism was based on oxidation and reduction reactions of induced charged carriers. Ultimately, in both reactions from water oxidation and dissociation of H_2O_2, hydroxyl radical could be produced, which are highly powerful and nonselective oxidizing agent. During the past few years, numerous efforts have been made for the discovery of new visible-light-responding semiconductors. Among the created groups of photocatalysts, the biggest part in the literature belongs to ferrates, halides, oxides, tungstates, sulfides, and vanadates. All the groups utilized recently in heterogeneous photocatalysis are listed in **Table 1**, while band gap values for selected groups of photocatalyst are shown in **Figure 1**.

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Recently, metal sulfides received much attention because their promising properties. CdS is one of the intensively investigated semiconductors owing to the narrow band gap (2.1–2.5 eV) in comparison with TiO_2 which may extend the utilization of visible light. For instance, Eskandari et al. [99] synthesized CdS by simple chemical precipitation method using mercaptoethylamine hydrochloride (MEA) as a capping agent. CdS showed higher photocatalytic activity than P25-TiO_2 in the photodegradation of methylene blue under blue LED and solar light irradiation. Reusability of the photocatalyst was checked five times; during the first three times, the activity decreased gradually, but in the last two cycles, they observed very sharp drop in photoactivity. Chen et al. [100] also observed higher activity of CdS in comparison with P25-TiO_2, after 60 min of UV irradiation nearly 95% of rhodamine B (RhB) was degraded. The band gap (2.24 eV) was calculated according to the UV–Vis absorption spectra [100]. Another very often mentioned material is ZnS. Chen et al. used ZnS rods as photocatalysts for the degradation of methyl orange (95% of MO was degraded after 20 min) and 2,4-dinitrophenol (54% of 2,4-NP was degraded after 20 min) under UV irradiation [105]. ZnS with a band gap equals to 3.84 eV exceeded activity of commercial P25-TiO_2. Chen et al. also proposed photocatalytic degradation mechanism of OM and 2,4-NP over ZnS under UV light. For this reason, EDTA-Na_2 and potassium iodide (KI) were introduced as the scavengers for h^+, isopropanol, and ethanol were used for $^{\bullet}OH$, and 1,4-benzoquinone for $^{\bullet}O_2^-$, respectively. They confirmed that the photocatalytic process proceeds analogously like for TiO_2, and thus, h^+ and $^{\bullet}O_2^-$ are the crucial in the degradation pathway under UV irradiation [105]. Chen et al. [115] applied simple wet chemical method for obtaining Bi_2S_3. The photocatalytic activity was measured by methyl orange degradation in the presence of UV light. After 4 h of irradiation, 97% of methyl orange was decolorized in the presence of Bi_2S_3 photocatalyst with specific surface area about 20 $m^2\ g^{-1}$ [115]. Luo et al. [116] performed Bi_2S_3 nanorods which exhibited superior activity than P25-TiO_2 in rhodamine B degradation under visible light ($\lambda > 420$ nm).

Another extensively examined groups are wide band gap oxides such as ZnO, WO_3, Nb_2O_5, and Bi_2O_3. Nanosized ZnO photocatalysts were synthesized by Liu et al. Obtained samples exhibited high activity in methyl orange degradation under UV light. After 30 min irradiation, the efficiency was nearly 100%. ZnO was proved to be very stable during 4 cycles. In many publications, some of the photocatalysts are perceived as a narrow band gap semiconductor such as Bi_2O_3, CeO_2, Fe_2O_3, and WO_3. This dispersion in the values of the band gap is inter alia due to different preparation method. Zheng et al. [166] synthesized WO_3 nanorod arrays by hydrothermal method, and the results showed that the pH value of the precursor solutions plays crucial role in the formation of the as-prepared structures, which leads to different band gap values. Ameen et al. [50] synthesized ZnO flower-like photocatalysts (E_g = 3.24 eV) which showed very high efficiency for crystal violet degradation under UV light irradiation. After 80 min of irradiation, about 96% was degraded. Mahmodiet al. [51] investigated the photocatalytic activity of ZnO on stainless steel support. The activity measurements were concerned with photoreduction of carbon dioxide in the presence of H_2, H_2O, and CH_4. It was noticed that TiO_2 has better photoreduction activity while the highest result for ZnO was achieved in the presence of CH_4 [51]. Li et al. [52] tested ZnO nanoparticles in the degradation reaction of methyl orange under UV light illumination. ZnO exhibited excellent degradation efficiency of methyl orange reached 97.84% after 30 min. Moreover, ZnO showed no significant loss of

photocatalytic activity during four repeated cycles [52]. Bismuth oxide with optical band gap value of 2.7 eV could be utilized as a visible-light-driven photocatalyst [79]. Iyyapushpam et al. prepared Bi_2O_3 by sol–gel method. Samples were calcined at two different temperatures (600 and 700°C), and the highest degradation efficiency was attained by semiconductor with higher crystallinity and specific surface area (sample calcined at 600 ◎C). The degradation percentage of methyl orange was found to be 76% [79].

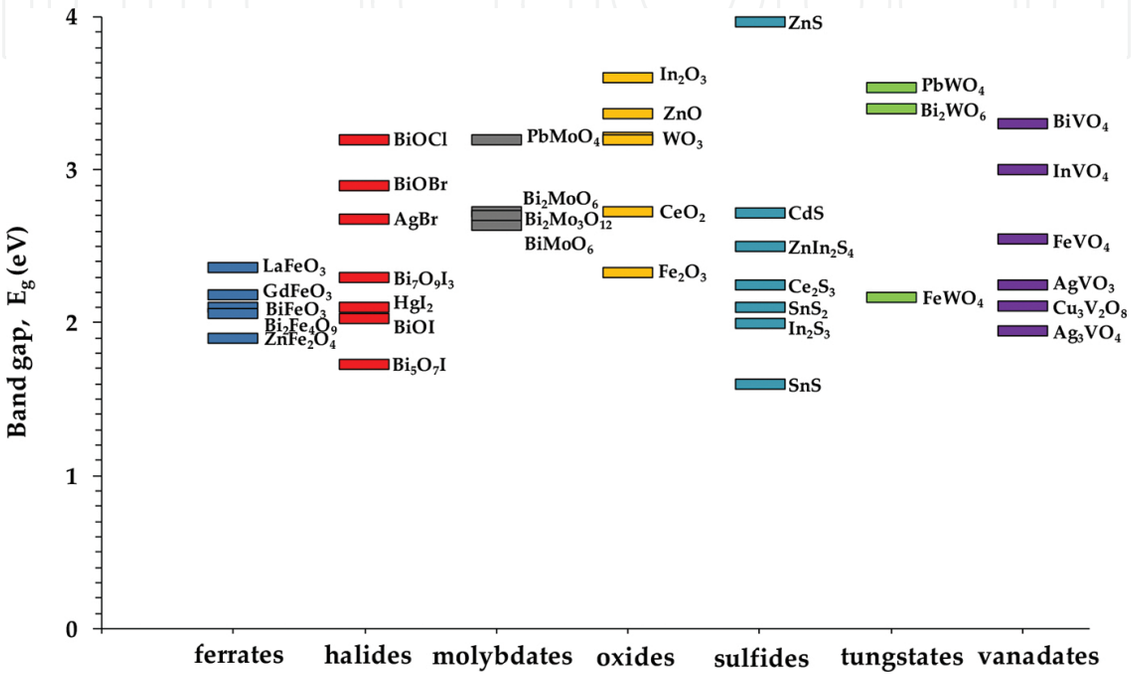

Figure 1. Band gap values for selected groups of photocatalyst collected based on the literature review.

Tungsten-based materials with a low band gap seemed to be promising candidate for the degradation of organic compound under visible light. For instance, Phattharanit et al. [128] obtained multi-layered flower-like Bi_2WO_6 by hydrothermal method and estimated activity of the powder in the degradation of rhodamine B under visible light. The results shown that after 360 min of irradiation, 88% of rhodamine B was degraded, which could be related to photosensibilization of semiconductor by dyes. In comparison, Saison et al. [129] synthesized Bi_2WO_6 with the band gap equals 2.9 eV and measured photocatalytic efficiency for Bi_2WO_6 and TiO_2. They observed relatively low activity of Bi_2WO_6 during rhodamine B and stearic acid degradation process under visible light. After calculation of the band diagram, Saison et al. explained that bismuth tungstate has inadequate band positions resulted in rapid recombination of excited pairs because electrons are not able to react with dioxygen.

Among the vanadates, $BiVO_4$ paid much attention because of the stability, nontoxicity, and relative high activity under the visible irradiation. In the most of the published papers, the photocatalytic activity of $BiVO_4$ was measured on model reaction of rhodamine B degradation [145–152]. Lin et al. [145] synthesized $BiVO_4$ (E_g = 2.36 eV) by simple hydrothermal

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method. After 180 min of visible light illumination, 100% of rhodamine B (λ >420 nm) was degraded. The stability was evaluated during four cycles, which indicated no significant decrease in photocatalytic activity [145]. Tan et al. [148] synthesized $BiVO_4$ powders by hydrothermal method. By the manipulation of reaction condition, different hierarchical structures such as octahedron, decahedron, spherical, and polyhedral were obtained [148]. The influence of pH values on the crystalline phase and morphology of the $BiVO_4$ powders was examined. The highest visible light photocatalytic activity for the rhodamine B degradation was achieved by sample prepared at pH 7.81 with specific surface area equals 5.15 m^2 g^{-1}. Lin et al. [145] also observed high activity of fishbone-like $BiVO_4$ for RhB degradation. The band gap around 2.36 eV was estimated from UV–Vis spectra. After 180 min irradiation, 100% of dye was removed.

Recently, encountered research about silver halides provides information about excellent activity, however, suffers by very low stability of AgX, which radically limited potentially reuse and application [38]. On the other hand, majority of the bismuth oxyhalides described in literature are perceived as a wide band gap semiconductor with high stability. Guan et al. [21] compared properties of two different kinds BiOCl nanoplates and ultrathin nanosheets. They indicated that these powders varied in band gap value, for BiOCl nanoplates E_g reached 3.25 eV while for nanosheets 3 eV. The higher photocatalytic activity for the degradation of RhB was observed in the case of ultrathin BiOCl. This phenomenon was explained by the creation of different defects which are formed after reducing the thickness of the nanosheets to the atomic scale [21]. Xiao et al. [35] prepared $Bi_7O_9I_3$ microsheets using simple microwave heating route. The degradation of bisphenol A induced *via* visible light irradiation was investigated. After 60 min of irradiation, almost 100% of bisphenol A was degraded. The reaction rate constant of the optimal sample was over 16 times greater than that of TiO_2-P25. $Bi_7O_9I_3$ microsheets revealed high mineralization capacity of bisphenol A and good stability during the recycle tests, implying a promising forecast in the industrial application of the photodegradation of organic pollutants. The mechanism analyses conducted by LC–MS suggested that the degradation of bisphenol A under visible light irradiation occurred predominantly by direct holes, and the main detected intermediates were hydroquinone and methyl 4-hydroxybenzoate [35].

Ferrates can be specified as a semiconductor with narrow band gap. There are several synthesis methods described in the literature used for ferrate preparation such as hydrothermal [11, 13, 14, 17], microwave hydrothermal [15], microwave [16], solid-state reactions [12], and solution combustion method [18]. These photocatalysts possess superior properties, and therefore, they seemed to allow their use in environmental purification. Due to magnetic properties of ferrates, they can be easily separated from reaction suspension. Shahid et al. reported high photocatalytic activity of $MgFe_2O_4$ in the degradation of methylene blue under UV (350 nm) and visible light (λ > 420 nm). In comparison with ferrate, TiO_2-P25 exhibited poor photocatalytic activity under visible light; after 50 min of irradiation, only 10% of dye was decomposed, whereas in the presence of $MgFe_2O_4$ even 95% of MB was degraded [12]. Tang et al. indicated that $LaFeO_3$ with band gap equals 2.36 eV and strong visible light absorption exhibited much higher activity in the MB degradation than

TiO_2-P25 [16]. Li et al. [11] have examined activity of $GdFeO_3$ in the degradation of 4-chlorophenol under visible light irradiation ($\lambda > 420$ nm). After 5 h of illumination, only 20% of 4-chlorophenol was removed by TiO_2-P25, while almost 85% was degraded over $GdFeO_3$. That obtained $GdFeO_3$ microspheres have characterized by broad absorption in visible light region and quite well photocatalytic stability after fifth run [11].

According to the literature data, many other groups of semiconductors are also used in heterogeneous photocatalysis, such as tantalates, titanates, molybdates, niobates, selenides, phosphates, stannate, carbonate, germanate, and cobaltites. Most of tantalate- and titanate-based materials can be activated only *via* UV light due to generally wide band gap, which can reached even 5.05 eV [167–169]. Nevertheless, it has been reported that these photocatalysts exhibited high activity which may be attributed to crystal structure of perovskites. Liang et al. [47–49]. Microcrystalline $AgNbO_3$ was synthesized by Wu et al. [47] by sol–gel method. The photocatalyst has proved to be stable for all recycle experiments. However, $AgNbO_3$ has shown high activity only for the decomposition of methylene blue and rhodamine B, and for 4-chlorophenol and methyl orange, there was no obvious drop of contaminants concentration. Bismuth niobate prepared by a facile hydrothermal route showed very good visible-light-induced performance for the removal of nitrogen monoxide [48]. It has been shown that the activity results of bismuth niobate are better than that for C-doped TiO_2, $InVO_4$, and BiOBr nanoplates [48]. Promising properties have been noticed also for molybdate-containing materials such as Bi_2MoO_6 with interesting layered perovskite structure [40]. Sun et al. [40] tested Bi_2MoO_6 with nanoplate like morphology prepared *via* hydrothermal method. The photocatalytic performance was evaluated by the degradation of rhodamine B and phenol under environment-friendly blue light emitting diode ($\lambda = 465$ nm) irradiation. They have found that after 30 min of illumination, almost 100% of rhodamine B was degraded, while in the presence of TiO_2-P25, only several percent of dye was removed even with addition of H_2O_2. Phenol was chosen as another model substance in order to exclude the influence of photosensitization. They have examined synergistic effect of photocatalysts and H_2O_2 for the phenol degradation. After 2 h of irradiation, the amount of phenol decreased up to 8% in over Bi_2MoO_6. They have concluded that Bi_2MoO_6 with narrow energy gap is able to respond directly to blue light emitting diode in contrast to TiO_2-P25 [40]. Bi et al. [41] have investigated the stability of Bi_2MoO_6, and during five-cycle experiments, they have not observed any obvious decrease in photocatalytic activity for rhodamine B degradation. Hipolito et al. [46] prepared bismuth molybdate photocatalysts using co-precipitation method. The activity of so obtained $Bi_2Mo_3O_{12}$ was further investigated for the removal of nitric oxide under UVA light irradiation. In comparison with Bi_2MoO_6 with a band gap equals 2.44 eV, the $Bi_2Mo_3O_{12}$ ($E_g = 2.7$ eV) turned out to be more active reaching around 30% more of NO removal. This dispersion of results could be attributed to higher surface area of $Bi_2Mo_3O_{12}$ and its abundant adsorption sites for NO adsorption [46].

Summarizing, it is possible to find several photocatalysts which provide better light-harvesting performance than TiO_2, and it is assumed that they can be good replacement of TiO_2. Unfortunately, there is still lack of precise research related to possibility of reuse the powders. It is

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needed to search new materials which will be environmental friendly, resistant to photocorrosion, and will not dissolve in water; otherwise, toxic metals and compounds such as Cd, Pb, or semiconductor sulfides will be useless for practical application. Most of the current research based on degradation of dyes, which can act as an organic semiconductor and participate in charge transition into CB under visible light irradiation. Therefore, the use of dye-photocatalysts system should be taken into consideration in the process of sewage treatment. Also, it should be noticed that the examination of activity in the degradation compounds such as 4-chlorophenol under UV light must be consider due to sensitivity to photolysis. Furthermore, results from the photolysis should be always placed with actual photocatalytic activity in order to make a reasonably comparison. There is still need for the standardization of photocatalytic measurements by utilizing the identical test equipment, photocatalysts dosage, kind and concentration of model compound, and other experiments condition, which allow making proper worldwide comparison of photocatalytic results.

Group	Semiconductor, Eg (eV)	Model pollutant	Irradiation range	Ref.
Antimonate	$GaSbO_4$ (3.7)	Acetone, salicylic acid	UV	[5]
	$AgSbO_3$ (2.6)	Rhodamine B	Vis	[6]
Carbonate	Ag_2CO_3 (2.46)	Rhodamine B, methyl orange, methylene blue	Vis	[7]
	$(BiO)_2CO_3$ (3.09–2.67)	Rhodamine B	UV	[8]
Cobaltites	$LaCoO_3$ (n/a)	Methyl orange	Vis	[9]
	La1–xBaxCoO_3 (2.80–2.21)	Formalachite green	Vis	[10]
Ferrate	$GdFeO_3$ (1.97–2.18)	4-Chlorophenol	Vis	[11]
	$MgFe_2O_4$ (n/a)	Methylene blue	Vis	[12]
	$BiFeO_3$ (2.1)	Rhodamine B	Vis	[13]
	$Bi_2Fe_4O_9$ (1.94–2.06)	Methyl orange	Vis	[14, 15]
	$LaFeO_3$ (2.36)	Methylene blue	Vis	[16]
	$ZnFe_2O_4$ (1.9)	Rhodamine B	Vis	[17, 18]
Germanate	$CeGeO_4$ (3.1)	Terephthalic acid	UV	[19]
	$ZnGa_2O_4$ (4.5)	Ethylbenzene, methyl orange, rhodamine B, methylene blue benzene, toluene	UV-Vis	[20]
Halides	BiOCl (2.87–3.2)	17 Alpha-ethinyl estradiol (EE2) and estriol, methyl orange, methylene green, rhodamine B, tetracycline hydrochloride	UV, Vis	[21–29]
	BiOBr (2.45–2.9)	Methyl orange, rhodamine B, tetracycline hydrochloride	UV, Vis	[22–24, 28, 30, 31]

Group	Semiconductor, Eg (eV)	Model pollutant	Irradiation range	Ref.
	BiOI (1.43–2.03)	Methyl orange, rhodamine B, tetracycline hydrochloride, 17 alpha-ethinyl estradiol (EE2), estriol	UV, Vis	[22–24, 32–34]
	$Bi_7O_9I_3$ (2.23–2.30)	Bisphenol-A	Vis	[35]
	Bi_5O_7I (1.73)	Rhodamine B	Vis	[36]
	HgI_2 (2.10)	Rhodamine B	Vis	[37]
	AgBr (2.58–2.68)	Methylene blue, methyl orange	Vis	[38, 39]
Molybdate	Bi_2MoO_6 (2.51–2.73)	Phenol, rhodamine B	Vis	[40, 41]
	$BiMoO_6$ (2.64)	Phenol, ibuprofen, rhodamine B	Vis	[42, 43]
	$PbMoO_4$ (3.1–3.2)	Methyl orange, rhodamine B , indigo carmine, orange G	UV, Vis	[44, 45]
	$Bi_2Mo_3O_{12}$ (2.73–2.70)	Nitric oxide	UV	[46]
Niobate	$AgNbO_3$ (2.9)	4-Chlorophenol, methyl blue, methyl orange, rhodamine B	Vis	[47]
	Bi_3NbO_7 (2.89)	Nitrogen monoxide	Vis	[48]
	$SnNb_2O_6$ (2.3–2.6)	Rhodamine B, methyl orange, malachite green	UV, Vis	[49]
Oxides	ZnO (2–3.37)	4-Chlorophenol, alizarin red S, CO2 reduction, hexane, methylene blue, reactive brilliant red K-2BP, methyl orange, rhodamine B, thionine, estrone, H2O2 generation, yellow 15	UV, UV-Vis	[50–70]
	ZrO_2 (n/a)	Direct Red 81 victoria Blue	UV-Vis	[71]
	WO_3 (2.4–3.21)	CO_2, CR, methyl blue, methylene blue, Orange II, rhodamine B	UV, Vis	[72–77]
	In_2O_3 (3.6)	Perfluorooctanoic acid	UV	[70]
	a-Fe_2O_3 (2.33)	Methylene blue	Vis	[78]
	Bi_2O_3 (1.3–2.73)	Cr(VI], aldehydes, congo red, rhodamine B, methyl orange	UV, Vis	[79–82]

Group	Semiconductor, Eg (eV)	Model pollutant	Irradiation range	Ref.
	CeO_2 (2.81–3.2)	4-Nitrophenol, indigo carmine, AO7, methylene blue, rhodamine B	UV, Vis	[83–86]
	Cu_2O (n/a)	Methyl orange	Vis	[87]
	Ga_2O_3 (n/a)	Methyl orange, rhodamine B	UV	[88]
	Nb_2O_5	Rhodamine B	UV, Vis	[89]
Phosphates	Ag_3PO_4 (2.35–2.47)	Bisphenol A, rhodamine B	Vis	[90–92]
	$BiPO_4$ (3.35–4.4)	Benzene, rhodamine B	UV	[93, 94]
selenides	ZnSe (2.9)	Methylene blue	Vis	[95]
Stannates	$CdSnO_3$ (4.4)	Benzene	UV	[96]
	Zn_2SnO_4 (n/a)	Reactive Red 141	Sunlight	[97]
	$ZnSnO_3$ (3.34)	Methylene blue	UV-Vis	[98]
Sulfides	CdS (2.1–2.5)	Methyl orange, methylene blue, methylene blue, rhodamine B	UV, Vis	[99–104]
	ZnS (3.37–3.97)	2, 4-Dinitrophenol, dinitrobenzene methylene green, rhodamine B, methyl orange	UV	[105–108]
	SnS_2 (2.1–2.25)	Methyl orange phenol, rhodamine B	Vis	[109–111]
	In_2S_3 (1.89–2.0)	DNA purine bases, formic acid, hydrogenation of 4-nitroaniline	UV, Vis	[112, 113]
	SnS (1.6–1.3)	Methylene blue	Vis	[114]
	Bi_2S_3 (n/a)	Methyl orange rhodamine B	UV, Vis	[115, 116]
	Ce_2S_3 (2.1)	Nitrobenzene reduction	UV, Vis	[117]
	$ZnIn_2S_4$ (2.72–1.92)	Benzyl alcohol	Vis	[118]
	$CdIn_2S_4$(n/a)	Inactivation of *Escherichia coli*	Vis	[119]
	$ZnIn_2S_4$ (n/a)	Methyl orange	Vis	[120]

Group	Semiconductor, Eg (eV)	Model pollutant	Irradiation range	Ref.
	$CdIn_2S_4$(n/a)	Methyl orange	Vis	[121]
Tantalates	$Sr_{0.25}H_{1.5}$ Ta_2O_6 H_2O (4.9)	Benzene oxidation	UV	[122]
	β-$BiTaO_4$ (2.45–2.65)	Methylene blue	Vis	[123]
	$Ba_4Ta_2O_9$ (5.05)	Methyl orange	UV	[124]
Titanate	$K_2Ti_6O_{13}$ (3.06–3.48)	Methyl orange	UV	[125]
	$FeTiO_3$ (2.54–2.58)	Rhodamine B	Vis	[126]
	$BaTiO_3$ (n/a)	Rhodamine B	Vis	[127]
Tungstates	Bi_2WO_6 (2.48–3.4)	2,4-Dichlorophenoxyacetic acid, methylene blue, rhodamine 6G, rhodamine B, tetracycline	UV, Vis	[128–139]
	$FeWO_4$ (2.17 eV)	Methyl orange	UV-Vis	[140]
	$SrWO_4$ (n/a)	Rhodamine B, rhodamine 6G	UV	[141]
	$Na_4W_{10}O_{32}$ (n/a)	Coumarin propan-2-ol	UV	[142]
	$NiWO_4$ (n/a)	Methylene blue	Vis	[143]
	$PbWO_4$ (3.54)	Acid orange II	UV	[144]
Vanadates	$BiVO_4$ (1.85–3.3)	Blue, ciprofloxacin, methylene phenol, rhodamine B	UV, Vis	[145–158]
	$AgVO_3$ (2.11–2.25)	Bisphenol A, rhodamine B	Vis	[159]
	Ag_3VO_4 (1.95)	Rhodamine B	Vis	[160]
	$InVO_4$ (2.4–3.0)	Ciprofloxacin, methylene blue, rhodamine B	Vis	[161–163]
	$FeVO_4$ (2.02–2.55)	Phenol	UV-Vis	[164]
	$Cu_3V_2O_8$ (2.11–2.05)	Methyl orange	Vis	[165]

Table 1. Selected representative photocatalysts and model substances used for activity measurements.

3. Single-semiconductor photocatalysts for water splitting

Photocatalytic water splitting, which is a process of decomposition of water into hydrogen and oxygen, is a promising method for obtaining clean and renewable energy. When light with an energy equivalent or greater than band gap of the semiconductor photocatalysts is irradiated,

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the electrons in the valence band are excited into the conduction band. The excitation of electrons creates holes in the valence band. These photogenerated electrons and holes trigger the redox reaction [170]. There are three main steps of photocatalytic water splitting: (1) The photocatalyst absorbs photon energy and electron–hole pairs are generated in the bulk; (2) the photo-excited charge carriers should separate and migrate to the surface with minimal recombination; and finally, (3) the free charge carriers triggers the oxidation and reduction reaction respectively at the surface, that is, the electron reduces H_2O to H_2 and the hole oxidized H_2O to O_2, respectively.

The production of hydrogen using a particulate photocatalyst has been examined by various research groups since 1972 and since that time scientists are trying to obtain the most efficient combination of semiconductors which will give payable level of hydrogen recovery [171]. In recent years, many various types of homogeneous and heterogeneous photocatalysts have been developed and intensively analyzed. Summary of studied heterogeneous photocatalysts used for water-splitting process are presented in **Table 2**. In fact, heterogeneous photocatalysis received lately more attention because of wider application scale. There is no single photocatalyst which can meet all the requirements to proceed efficient water-splitting process for H_2 production. The success is not only in careful selection of semiconductor photocatalysts but also their optimal surface structures. Additionally, a suitable band gap, matching energy band for H_2 and O_2 evolution, high quantum efficiency and stability are also important. The main task of scientists is to develop the composition of semiconductor materials, which will carry out suitable optical absorption, reduction, and oxidation abilities and increase efficiency in solar energy conversion [197]. It is thought that co-catalyst components such as Pt, Ni, Rh, and Ru can promote H_2 evolution because of their lower over potentials, while they are also active for the oxygen reduction reaction (ORR), which corresponds to the reverse of the water-splitting reaction [36]. Positive water splitting was also observed in the presence of co-catalysts such as Pt, Pd, and Rh or a metal oxide such as NiO, RuO_2, and Cr_2O_3, which are loaded onto the photocatalyst surface to produce active sites for water reduction reaction [171]. Following the assumption of water-splitting process for hydrogen production, we chose these examples, which demonstrate the best perspectives.

Following the idea of development of better photocatalysts for water splitting in visible light spectrum, we chose the most promising examples by comparing energy band gaps and hydrogen production rate, not considering TiO_2 photocatalysts. The apparent quantum yield (AQY) for the production of hydrogen and oxygen gas can be estimated by the following Equation (1):

$$\mathrm{AQY}(\%) = \frac{\text{number of reacted electrones}}{\text{number of incident photons}} \times 100 \tag{1}$$

Liao et al. [180] conducted water-splitting process using cobalt oxide particles. The photocatalysts were obtained from nonactive CoO micropowders with two distinct methods —femtosecond laser ablation and mechanical ball-milling. Water-splitting experiments were performed in air-tight flasks with CoO nanoparticles suspended in neutral water. Generation

of hydrogen and oxygen was measured by a gas chromatograph (GC) equipped with a thermal conduction detector (Gow-Mac). High photocatalytic activity of the nanoparticles was analyzed by electrochemical impedance spectroscopy (SRS residue gas analyser, RGA200), which comes from a significant shift in the position of the band edge of the material with regard to water redox potential. The conduction band of CoO micropowder is located below the hydrogen—evolution potential what leads to inactivity in water splitting process. A mass spectrometer was also used to identify isotope gas species from water splitting. Received CoO nanoparticles can decompose pure water under visible light irradiation without any co-catalysts or sacrificial reagents with the hydrogen production assessed for 71,429 μmol/h g^{-1} [180].

Twinned $Cd_{0.5}Zn_{0.5}S$ anisotropic nanocrystals (called nanorods) with controllable aspect ratios and a high proportion of long-range ordered twin planes were investigated by Liu et al. [195]. Between the planes in the crystal, the zinc–blende (ZB) and wurtzite (WZ) were generated. The TEM image revealed that nanorods consisted of a high density of stacking faults with parallel distribution, which were coherent twin boundaries. During the process between the segments of ZB and WZ, the type II staggered band was created which in particular dimension cause the generation of myriad homojunctions. This formation leads to photocatalytic hydrogen production with a remarkable QE of 62% and 25,800 μmol/h g^{-1}. Different combinations of the same elements were investigated by Li et al. [194], where the solid solution of $Zn_{1-x}Cd_xS$ was analyzed. Obtained structures characterized with a small crystallite size and precise band structure. The photocatalytic hydrogen production experiment was performed at ambient temperature and atmospheric pressure, using 350 W xenon arc lamp through a UV cut-off filter ($\lambda > 400$ nm). Study revealed that sample containing $Zn_{0.5}Cd_{0.5}S$ is the most promising in terms of hydrogen production with the rate of 7420 μmol/h g^{-1}, which is much more than amounts produced with the pure CdS or ZnS samples.

Group	Semiconductor, Eg (eV)	Irradiation range(nm)	H_2 production rate (μmol/h g^{-1})	O_2 production rate (μmol/h g^{-1})	Apparent quantum yield (%)	Ref.
Sulfides	CdS (2.4)	λ>420	25	n/a	n/a	[172]
	$CaIn_2S_4$(1.84–168)	λ>420	2.64	n/a	n/a	[173]
	Sb_2TiS_5 (1.87)	UV	10.4	n/a	n/a	[174]
	$(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ (2.72–1.92)	λ>420	1750	n/a	12.8	[175]
	$ZnIn_{2.3}S_{4+y}$ (4.894)	λ>420	363	n/a	n/a	[176]
	Cu_3SnS_4(1.38)	λ>420	1100	n/a	3.9	[177]
	$Mn_{0.24}Cd_{0.76}S$(2.28)	λ>420	10,900	n/a	9.5	[178]
Oxides	Ta_2O_5 (3.9)	λ>420	7100	n/a	n/a	[179]

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Group	Semiconductor, Eg (eV)	Irradiation range(nm)	H_2 production rate (μmol/h g^{-1})	O_2 production rate (μmol/h g^{-1})	Apparent quantum yield (%)	Ref.
	CoO (2.6)	λ>420	71,429	35 714	5	[180]
	Fe_2O_3 (2.3)	λ>420	n/a	3	n/a	[181]
Vanadates	$InVO_4$(3.0)	λ>420	14.16	n/a	n/a	[182]
	$Ag_2Sr(VO_3)_4$(2.4)	λ>420	n/a	8,1	n/a	[183]
	$Sr(VO_3)_2$ (2.7)	λ>420	n/a	12	n/a	[183]
Halides	LaOF (4.7)	UV	27	n/a	n/a	[184]
Tantalites	$NaTaO_3$ (4.1)	UV	3106	n/a	n/a	[185]
	$Cd_2Ta_2O_7$ (3.35)	UV	173	86.3	n/a	[186]
Ferrates	$GaFeO_3$ (2.02-2.18)	λ>395	289	n/a	n/a	[187]
	$LaFeO_3$ (2.07)	λ>420	3315	n/a	n/a	[188]
	$ZnRh_2O_4$(1.2-2.2)	UV, Vis	500	n/a	27	[189]
	$NiFe_2O_4$ (1.7)	λ>420	1.97	n/a	0.07	[190]
	Ta_3N_5 (2.08)	λ>420	410	n/a	–	[191]
	$ZnIn_2S_4$(2.59-2.83)	λ>420	220.45	n/a	13.16	[192]
	$Bi_{0.5}Na_{0.5}TiO_3$ (2.82-2.92)	UV-Vis	324.5	n/a	3	[193]
	$Zn_{0.5}Cd_{0.5}S$ (2.45)	λ>420	7420	n/a	9.6	[194]
	$Cd_{0.5}Zn_{0.5}S$ (2.62)	λ>420	25,800	n/a	62	[195]
	$K_{0.5}La_{0.5}Bi2Ta_2O_9$/ $K_{0.5}La_{0.5}Bi_2Nb_2O_9$ (3.22-3.9)	UV	5.9–531	3.4 – 182	n/a	[196]

Table 2. Non-TiO_2 single photocatalysts for water splitting in UV/visible light spectrum.

Solid solutions of $Mn_{1-x}Cd_xS$ were fabricated by hydrothermal route in low temperature (130°C) by Liu et al. [178]. The H_2 evolution from water was performed under 300 W Xe lamp. 0.025 g of powder photocatalyst was dispersed in a pyrex cell with aqueous solution of 0.1 M Na_2S and 0.5 M Na_2SO_3. The characterization of samples revealed that with growing value of *x*, the rate of hydrogen increases. The highest value of H_2 production presented $Mn_{0.24}Cd_{0.76}S$ which in fact exceeds rate for pure CdS. The procedure was continued, and after third turn, the amount of H_2 decreased, what can be the result of consumption of the sacrificial agents—Na_2S and Na_2SO_3. The examined solution shows good photocatalytic stability and anti-

photocorrosion capability during water-splitting reaction what can be a promising discovery for the future. There are some examples of semiconductors which generate smaller amount of hydrogen than compounds described above; however, it still have potential for further studies in water-splitting area. $ZnRh_2O_4$with rate of hydrogen production of 500 μmol/h g^{-1} was studied by Takimoto et al. [189]. The measurements were conducted under monochromatic light and full Xe light lamp in wide range of wavelengths ($400 < \lambda \leq 770$ nm) with an intensity of 10 μW/cm^2. The amount of hydrogen produced is much less than in case of other presented semiconductors, but it is extraordinary because of a high efficiency yield (12%) at a wavelength of $\lambda = 770$ nm. The study revealed that this photocatalyst should be deeper investigated mainly because of possible usage in a wide range of light spectrum both visible and infrared light what is quite unique [189].

The overall compilation of already conducted experiments shows that there is a big potential for hydrogen production in photocatalytic water splitting in visible light range. The values of energy band gap indicate that non-TiO_2 single photocatalysts should be good candidates used in hydrogen production process without light limitations. The most promising results were obtained for different combinations of Cd composite what can lead to further studies in this particular area. Unfortunately, it is clear that single photocatalysts are not as efficient as should be expected. This is the reason why attention of researchers has been moved to more promising topics as the binary and ternary compounds or doping processes. Moreover, the demonstration of the simultaneous evolution of H_2 and O_2 is extremely difficult in the two-step water-splitting system because backward reactions easily proceed over each photocatalyst.

4. Binary composite photocatalysts

There are number of different types of photocatalytic materials, which are inefficient or not active during the light-mediated process of pollutants degradation. Various methods are used to improve the oxidation ability of photocatalysts in purification systems, such as doping with nonmetal ions, rare-earth metals, noble metals and transition metal ions, surface modification, dye sensitizing [198]. Among them, enhancing the photocatalytic activity can be achieved by coupling single semiconductors in composites.

Synthesis of new 3D semiconductor composites creates the opportunity to use materials with lower energy activation as a photocatalysts. Furthermore, application of the composite structures can lead to photocatalysts activated by low powered and low cost irradiation sources (such as LEDs or black fluorescent UV lamps) and can be used both in air and water purification systems. Therefore, it is important to develop convenient, low-cost, and environmental-friendly methods to synthesize high-quality photocatalysts.

Nowadays promising idea based on combining wide band gap semiconductors with narrow band gap materials. The narrow band gap photocatalyst can be excited in visible light region. The photogenerated holes and electrons can be transported to the wide band gap semiconductor and photo-excited with lower energy transfer. Furthermore, the nanocomposites materials exhibit improved quantum efficiency. Therefore, composites with narrower band

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gap semiconductors have been developed to extend the photo-absorption range, facilitate the separation of the photo-induced carriers, and extend the activity into the visible light region. A composite of two photocatalysts with surface contact formed a heterojunction which limits the electron transfer. There are three main processes which may lead to consumption of the photo-induced electrons: (*i*) volume recombination (recombination with produced holes inside the photocatalyst), (*ii*) surface recombination (reaction with spices on surface of the particle, and (*iii*) the H_2 production as a result of reaction with protons.

4.1. Photo-excitation mechanisms of binary composites

In general, there are three different mechanisms of binary composite photo-excitation under ultraviolet and visible light. Most of the current research is focused on efficiently suppression of the recombination processes. Summary of studied composites and possible mechanisms of photo-excitation (named mechanism A, B, and C) are presented in **Table 3**. During the irradiation, both photocatalysts can be excited with photogenerated charge carriers depending on the band gap energy (E_g). Usually under visible light irradiation, the electrons produced in narrow band gap semiconductor (named semiconductor A) with less positive conduction band (CB) can be transferred quickly to the more positive CB of the photocatalyst with the wider band gap (semiconductor B). In the other hand, the photo-excited holes from semiconductor B could be shifted easily into the valence band (VB) of the semiconductor A. The each position of conduction and valence band in photocatalysts according to the mechanism A is presented in **Figure 2a**. The $Ag_3PO_4/ZnFe_2O_4$ composite was synthesized by Chen et al. *via* a solvothermal-liquid phase deposition method [230]. The photocatalytic activity test was performed as a 2,4-dichlorophenol degradation under visible light irradiation. During the process using $Ag_3PO_4/ZnFe_2O_4$ with mass ratio 9:1, 95% of the pollutant was decomposed after 70 min of irradiation (two and three times higher than result for single photocatalyst). It was found that the conduction and valence band of $ZnFe_2O_4$ is more negative than CB and VB of Ag_3PO_4. Structure formation of $Ag_3PO_4/ZnFe_2O_4$ material resulted in expanding the spectral responsive range of Ag_3PO_4. High-effective photocatalyst under Vis light was obtained by combining the single $BiVO_4$ with $FeVO_4$ [222]. The heterojunction composite photocatalysts was stable in photocatalytic removal of metronidazole in aqueous phase. Moreover, enhanced oxidation properties resulted from the fast transfer of photogenerated charge carriers. The optimal weight ratio in Ag_3PO_4/BiOBr composite was equal to 0.7. The process of energy bias generation at heterojunction plays significant role in electron and hole pair transfer. The rate of removal rhodamine B under visible light was maintained at 95% after 6 recycling processes [224].

In view of the internal field between semiconductors, in some composites used for photodegradation under visible light, only electron transfer exists without hole migration in the valence band (the process is named mechanism B, see **Figure 2b**) [199, 213, 214, 218, 219]. Xu et al. [213] synthesized CdS/MoS_2 composite active under visible irradiation range. The favorable heterojunction between CdS and MoS_2 extended lifetime of the charge carriers [213, 214]. The same type of mechanism was observed for CdS/SnO_2 photocatalyst where electrons shift from cadmium sulfides conduction band to the thin oxides band [199]. Consequently, the charge carriers in junction between semiconductors were effectively separated *via* one-step process.

All types of described mechanisms (mechanism A, B, and C) are caused by the presence of heterojunctions among different semiconductors that enhance the separation of the photo-generated electron–hole pairs, hindering their recombination.

Whereas, under the ultraviolet light illumination, both semiconductors simultaneously or the semiconductor with wider band gap in the composite could be excited. The mechanism of photo-excitation in binary composites was investigated by Hamrouni et al. Two photocatalysts: $ZnO/ZnWO_4$ and ZnO/SnO_2 prepared by a facile sol–gel method were examined in the photocatalytic decomposition of 4-nitrophenol under ultraviolet light range [200]. It was found that the local heterojunction between the photocatalysts pair facilitates the separation of the photogenerated e^-/h^+ pairs (mechanism C, see **Figure 2c**). A photocatalysts with enhanced electron–hole separation and excellent photocatalytic performance was investigated by Duo et al. [215, 217]. The methyl orange solution and Rhodamine B were used as a model substance in degradation under simulated sunlight. Both composites $BiPO_4/BiOCl$ and $BiPO_4/BiOBr$ exhibited significantly higher activity in dyes elimination than single semiconductors [216, 217].

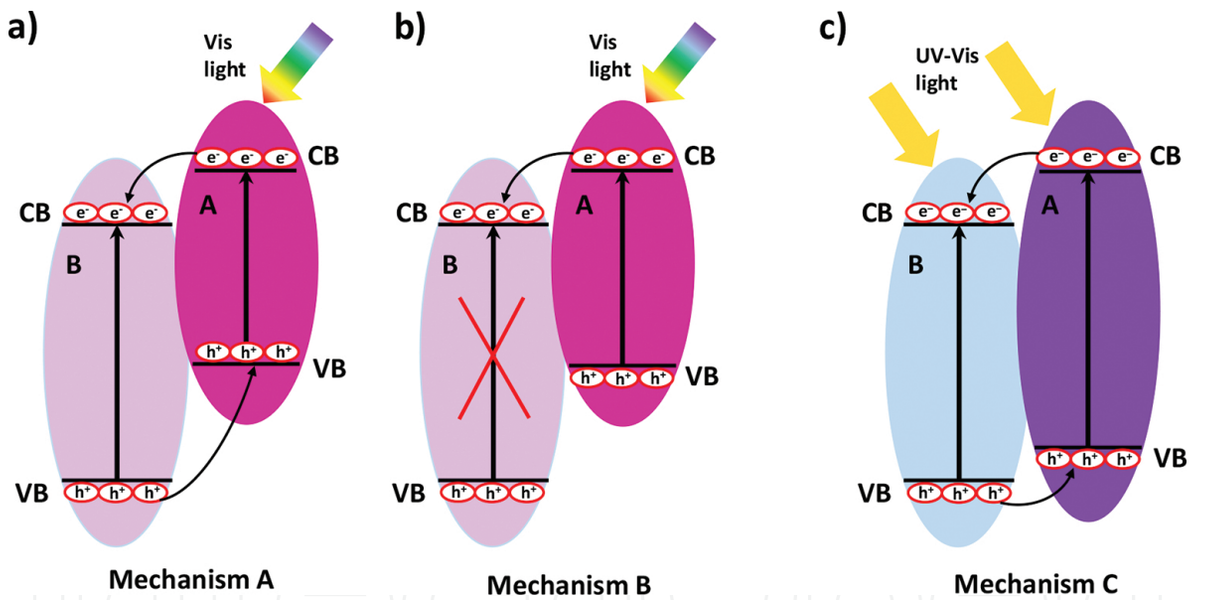

Figure 2. Possible mechanism of semiconductors composite photo-excitation: (a) Mechanism A under UV–Vis light, (b) Mechanism B under Vis light, and (c) Mechanism C under Vis light.

Semiconductor A	Semiconductor B	Irradiation range	Excitation mechanism	Ref.
CdS (2.17)	SnO_2 (3.3; 3.55)	Vis	Mechanism C	[199]
ZnO_2 (3.2)		UV	Mechanism A	[200]
ZnO_2 (3.2)	$ZnWO_4$ (3.14)	UV	Mechanism A	[200]
ZnO_2 (3.2)	Bi_2O_3 (2.8; 2.38; 2.75; 2.89)	UV	Mechanism A	[201]
$NaBiO_3$ (2.36)		Vis	Mechanism B	[202, 203]

Semiconductor A	Semiconductor B	Irradiation range	Excitation mechanism	Ref.
$BaTiO_3$ (3.18)		UV	Mechanism A	[204]
$NaBi(MoO_4)_2$ (3.08)		Vis	Mechanism B	[205]
Bi_5O_7I (3.13)		Vis	Mechanism B	[206, 207]
Bi_2O_3 (2.9)	Bi_2WO_6 (2.8; 3.1; 2.97)	Vis	Mechanism B	[208]
$ZnWO_4$ (3.75)		UV-Vis	Mechanism A	[209]
CeO_2 (2.58)		UV-Vis	Mechanism A	[210]
$Bi_{12}TiO_{20}$ (2.57		UV-Vis	Mechanism A	[211]
CdS (2.22)	Bi_2MoO_6 (2.8)	Vis	Mechanism B	[212]
CdS (2.25)	MoS_2 (1.75)	Vis	Mechanism C	[213, 214]
BiOBr (2.62)	$BiPO_4$ (4.16; 3.83; 4.11)	Sunlight, Vis	Mechanism A, Mechanism C	[215, 216]
BiOCl (3.12)		Sunlight	Mechanism A	[217]
Bi_2MoO_6 (2.53)		Vis	Mechanism C	[218]
Bi_2MoO_6 (2.71)	$BiIO_4$ (3.02)	Vis	Mechanism C	[219]
Cu_2O (2.5)	BiVO4 (2.0; 2.47)	Vis	Mechanism B	[220, 221]
$FeVO_4$ (2.05)		Vis	Mechanism B	[222]
$BiVO_4$ (2.49)	$Bi_4V_2O_{11}$ (2.22)	Vis	Mechanism B	[223]
Ag_3PO_4 (2.36)	BiOBr (2.74; 3.13; 2.76; 2.81)	Vis	Mechanism B	[224]
BiOI (2.45; 1.74; 1.72)		Vis	Mechanism B	[225–227]
BiOI (1.90)	WO_3 (2.60)	Vis	Mechanism B	[228]
WO_3 (2.68)	H_2WO_4 (2.45)	Vis	Mechanism B	[229]
$ZnFe_2O_4$ (1.88)	Ag_3PO_4 (2.44)	Vis	Mechanism B	[230]
Ag_3VO_4 (2.05)	Co_3O_4 (2.07)	Vis	Mechanism B	[231]
	$ZnFe_2O_4$ (1.90)	Vis	Mechanism B	[232]
$Ag_4P_2O_7$ (2.63)	AgBr (2.6)	Vis	Mechanism B	[233]
AgBr (2.64)	ZnO (3.0; 3.22; 3.3; 3.37; 3.26)	Vis	Mechanism C	[234–237]
Ag_2S (1.0)		Sunlight	Mechanism A	[238]
AgI (−)		Vis	Mechanism C	[239]
AgI (2.51)	Ag_2CO_3 (2.30)	Vis	Mechanism B	[240]
$SmCrO_3$ (2.7)	$Sm_2Ti_2O_7$ (3.2)	Sunlight	Mechanism A	[241]
In_2O_3 (2.90)	α-Fe_2O_3 (2.03)	Vis	Mechanism B	[242]

Table 3. Summary of studied composites and possible mechanisms of photo-excitation.

4.2. Ternary composite photocatalysts

Based on the literature data, it could be expected that ternary semiconductor composites provide an opportunity for multi(two)-photons excitation of photoactive materials with lower energy photons and utilization of heterojunction to drive electronic processes in the desired direction. Consequently, the selective photo-excitation of localized electronic states to gain better selectivity should be achieved [243].

The composite of $KTaO_3$–CdS–MoS_2 with different molar ratio was synthesized by Bajorowicz et al. [244] *via* hydrothermal method. The micromaterials were prepared under strictly controlled conditions of temperature and pressure depending on the material type. Hydrothermal method does not require a calcination step and is easy to carry out technological conditions. Various structures of the photocatalysts such as cubic, hexagonal, nanoleaf, and microspheres were obtained. Calcination at 500°C for 3 h and hydro/solvothermal mixed solutions method were used to combine single semiconductors. The highest phenol photodegradation (80% under UV–Vis and 42% under Vis light) was observed for the $KTaO_3$–CdS–MoS_2 at the 10:5:1 molar ratio. In the toluene oxidation process under ultraviolet light, the powder exhibit very good stability and efficiency during four measurement cycles (activity reached about 50%) [244]. A comparatively to SnO_2/ZnO/$ZnWO_4$ composites in this case probably a two-photon excitation occurs under UV–Vis irradiation [200, 244]. The $KTaO_3$/CdS/WO_3, $KTaO_3$/CdS/MoS_2, $KTaO_3$/CdSe/$SrTiO_3$ composites preparing by various route with different molar ratio were compare in photocatalytic degradation of gaseous toluene under ultraviolet light. The results suggest that the structure, morphology, and photoactivity depend on the type and molar content of additional semiconductors as well as on the preparation method. Samples prepared by one-pot hydrothermal synthesis had higher surface area. Unfortunately, the morphology was not well developed and crystal structures of each single semiconductor were not formed. In four subsequent cycles, the photoactivity using the $KTaO_3$/CdS/MoS_2 (10:5:1) ranged 60% after 60 min of irradiation [245]. Hong et al. found that highly enhanced photocatalytic activity is due to synergistic effects of heterostructured ZnS/CuS/CdS material which can improve light absorption and charge carriers flow. The photocatalyst was stable under applied conditions (under solar irradiation 1 kW/m^2, AM 1.5 G) in H_2-production from a water splitting. The optimum ratio of loading the Cu equal to 0.81 wt% and Cd equal to 14.7 wt% was selected. The authors believed that the solar light causes electron excitation and separation in CdS (because of relatively narrow band gap), and consequently, efficient separated carriers flow to CuS conduction band during the holes from the ZnS were transferred to the valence band of CdS. Additionally, enhancing the H_2 production may result from the interfacial charge transfer between valence band of ZnS and CuS and partial reduction of CuS to Cu_2S [246]. It was observed that for some composites (i.e., ZnO/AgBr/Ag_2CrO_4), two semiconductors are excited and act as electron donors for wider photocatalyst. Reduction processes of the pollutant occur in the conduction band of the electron acceptor, whereas the electron donors will responsible for the oxidation reactions on valence band [247]. On the other hand, other mechanism, where ZnO plays a role of electron donor, was observed for SnO_2/ZnO/$ZnWO_4$ composite [200]. The SnO_2/ZnO/$ZnWO_4$ composite was examined under UV irradiation in 4-nitrophenol degradation process. Generated

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electrons in the conduction band of ZnO are shifted to those of SnO_2 and $ZnWO_4$; meanwhile, holes may be transferred from the valence band of SnO_2 and $ZnWO_4$ to that of ZnO. It was established that the elimination efficiency of a pollutant depends on adsorption level on the photocatalytic surface and ability to react with the photogenerated charge carriers. The amount of each semiconductors in the photocatalytic material determined the photocatalytic activity [200]. Enhanced photocatalytic activity in rhodamine B degradation process was observed for In_2O_3/AgBr/Bi_2WO_6 ternary composite (see structure on **Figure 3a**) [248]. Photocatalyst has exhibited higher activity under UV, visible, and simultaneous sunlight in comparison to single Bi_2WO_6 semiconductor, binary AgBr/Bi_2WO_6 material and pure P25. Proposed mechanism based on electrons transfer from In_2O_3 with the widest band gap to AgBr and consequently transition e^- from AgBr to Bi_2WO_6, which is semiconductor with the least negative CB in composite. The generated O_2^{*-} radicals in the conduction band plays a role in oxidation processes of pollutant. The produced holes (h^+) in the VB of semiconductors can oxidize the water molecules on the photocatalyst surface and leads to produce hydroxyl radicals (*OH) which are able to degrade dyes into CO_2 and H_2O (see **Figure 3b**.) [248]. A various materials are tested in different model photocatalytic reactions and under various conditions. Therefore, it is intricate to summarize and compare properties and photoactivity of new 3D structures. Some already investigated combinations of ternary composites are presented in **Table 4**.

Semiconductor I, Eg (eV)	**Semiconductor II, Eg (eV)**	**Semiconductor III, Eg (eV)**	**Irradiation range**	**Ref.**
ZnO (3.2)	AgBr (2.6)	Ag_2CrO_4 (1.8)	Vis	[247]
ZnO (−)	Ag_3VO_4 (2.1)	Fe_3O_4 (−)	Vis	[249]
ZnO (3.2)	AgI (2.8)	Fe_3O_4 (0.1)	Vis	[250]
ZnO	Ag_1	Ag_2CrO_4	Vis	[251]
SnO_2 (3.2)	ZnO (3.55)	$ZnWO_4$ (3.14)	UV	[200]
CdS (2.25)	PbS (1.2–1.5)	ZnO (3.36)	Vis	[252]
ZnS	CuS	CdS	Sunlight	[246]
Fe_3O_4 (−)	AgBr (−)	ZnO (3.2)	Vis	[253]
Fe_3O_4 (0.1)	SiO_2 (8.9)	Bi_2MoO_6 (2.71)	Vis	[254]
BiOBr (2.72)	SiO_2 (−)	Fe_3O_4 (−)	UV-Vis, Vis	[255]
Bi_2S_3	Bi_2O_3	$Bi_2O_2CO_3$	Vis	[256]
In_2O_3 (3.75)	AgBr (2.6)	Bi_2WO_6 (2.76)	UV, Vis, sunlight	[248]
Ag_2O	Ag_3VO_4	$Ag_4V_2O_7$	Vis	[257]
PdS (−)	CdS (−)	NiS (−)	Vis	[258]

Table 4. Compilation of ternary composites and photo-excitation irradiation range.

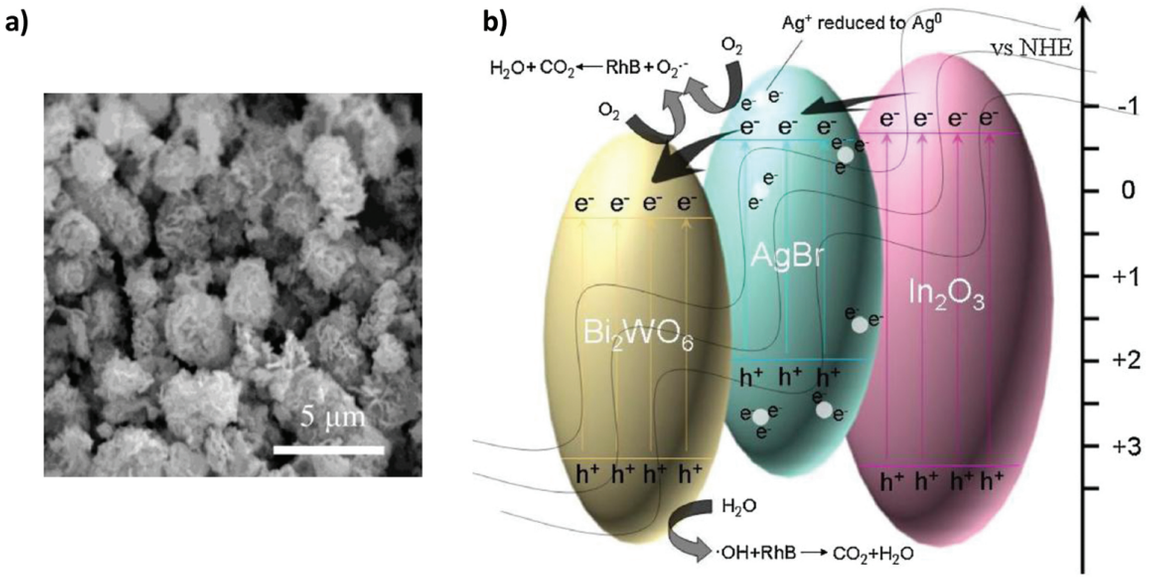

Figure 3. Ternary In_2O_3/AgBr/Bi_2WO_6 photocatalyst (a) Scanning Electron Microscope image, (b) Possible mechanism of photo-excitation in composite structure. Adapted with permission from Ref. [248].

Concluding the mechanism of photo-excitation of ternary composites, it is still not well understood. According to Serpone theory, photo-excitation of components A and B would be very efficient because the two nanomaterials are activated through their fundamental absorption band [243, 259]. There are some interactions which probably occur, while the irradiation excites photocatalyst. The process could be sophisticated and need further investigation.

5. Conclusions

Semiconductor photocatalysis affords a potential solution to the problems of energy shortages and environmental pollution. However, photo-efficiency of the most single semiconductors is limited because of the rapid electron–hole recombination. Therefore, the development of efficient visible-light-driven photocatalysts is a major challenge in this field. The photocatalytic activity of semiconductor photocatalysts depends on its physical and chemical properties, and additionally, depends on the recombination of photo-excited electrons and holes occurs at crystal lattice defects. Fortunately, the coupling of two or three semiconductors with different band gap values could improve the stability, necessary for practical applications and could extend the energy range used for excitation. Especially, the fabrication of a *p–n* junction is believed to be the most effective because of the existence of an internal electric field. Moreover, the hybrid photocatalyst can benefit from the synergistic effects such as enhanced light-harvesting ability, efficient photogenerated electron–hole separation, and improved photostability, and thus, the photoactivity is remarkably improved. However, it should be noted that the reason for the improvement of composite photocatalyst is not only due to the effects described above but also due to enhancement of surface acidity or alkalinity and the surface

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population of OH groups, which can promote the adsorption of reaction substrates and facilities the generation of hydroxyl radicals (•OH), respectively.

Based on the literature data, it can be concluded that most of the photocatalytic investigations are focused on dyes oxidation (such as methyl orange, rhodamine B, methylene blue, and malachite green) as the model degradation process of pollutants. According to Ohtani recommendation, the use of organic dyes as a model compound for photocatalytic decomposition reaction, enabling the feasible determination of photocatalytic activity, especially using spectrophotometric analysis [260]. He indicated at least three reasons for its inappropriateness. One is that the dye molecules absorb photons, especially in the visible light range, and thus photo-excited electrons may be injected into photocatalyst particles as has been suggested by the action spectrum similar to the absorption spectrum of the dye. Another reason is that the absolute molar amount of dye contained in the reaction system can be much smaller than that of a solid photocatalyst. Since the photo-absorption coefficient of dyes is generally large, for example, $>10^5$ mol^{-1} L cm^{-1}, the concentration can be 10^{-5} mol L^{-1} and the absolute molar amount can be 10^{-6} mol when the volume of the solution is 100 mL. The third reason is that the mechanism of dye degradation is so complicated that efficiency of the photocatalytic reaction cannot be measured.

In this point of view, there are still few works investigated on the photoactivity of composite photocatalyst shows enhanced photocatalytic activity for water splitting and organic degradation except dyes. Additionally, to better understand the properties of semiconductor composites and their role in photocatalysis processes, novel preparation methods need to be developed. Moreover, photocatalytic mechanisms and relationships among the structures forming the composites, surface, and crystal properties and photocatalytic activity should be thoroughly investigated and clarified.

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